

UDC 666.3-12

CERAMIC FROM NANOPOWDERS AND ITS PROPERTIES

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Translated from *Steklo i Keramika*, No. 12, pp. 10 – 13, December, 2008.

The possibilities for obtaining ceramic from nanodispersed silicon dioxide and hydroxyapatite powders are examined. Ceramic with fine-granular (3 – 10 μm) structure has been obtained. Transmission and scanning electron microscopy and x-ray phase analysis are used to study the properties of the initial nanopowder and ceramic. The glassy materials obtained from Tarkosil (silicon dioxide) powder are transparent in the ultraviolet range. Strong ceramic samples of hydroxyapatite with grains and pores smaller than 1 μm or less and with open porosity uniformly distributed throughout the volume have been obtained. The results of the investigation could be useful for developing medical implants based on hydroxyapatite and ceramic membranes with controllable porosity.

The properties of materials consisting of nanoparticles (smaller than 100 nm) differ substantially from the properties of coarse-grain materials. The electronic structure, conductivity, reactivity, melting temperature, and mechanical characteristics all change. For example, nanopowders of metals obtained in an electron accelerator (RF Patent No. 2067077) [1] by evaporating the initial materials exhibit high catalytic characteristics [2], and nanosize silicon powders exposed to ultraviolet radiation re-radiate in the visible blue-green part of the spectrum [3].

One of the directions of nanotechnologies is the development of nanoceramics from nanopowders. Special efforts are being made to keep the smallest possible grains in the final product. Apparently, this direction of work is one that could result in the required progress in materials science and technologies.

It is known that the development of dislocations is held back on grain boundaries. Correspondingly, the smaller the grains of ceramic and the more extended the grain structure, the stronger the ceramic is. Consequently, obtaining a fine-grain ceramic with a uniform structure makes it possible to expand its applications in many fields, for example, the structural components of motors, cutting tools, bioceramics (as a coating for implants), corrosion and wear-resistant coatings, insulators with high dielectric characteristics, and so forth.

Aside from solving the problems of strength, preserving the grain size is a determining factor in the use of nanocom-

ponents, specifically, nanodispersed powders, for developing artificial ceramic materials with open porosity. This field is of great importance for developing ultramembranes as well as biocompatible ceramic implants for medical prostheses. However, the development of real technologies encounters a number of specific problems (specifically, the presence in nanoparticles of stable nanoparticle agglomerates which are difficult to break up [4, 5]). Progress in this direction requires making the required efforts toward selecting powders as well as testing the main stages of the production of ceramics with open porosity from nanocomponents.

The objective of our work is to obtain from nanodispersed silicon dioxide SiO_2 and hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ powders a strong ceramic with small grain size (3 – 10 μm), and for hydroxyapatite powder (which is, specifically, a biocompatible material [6]), in addition, with open porosity with controllable pore size.

The powders used were obtained by evaporating the initial materials in an electron accelerator followed by condensation of the material in the form of nanodispersed particles by means of the method described in the RF patent No. 2067077 and in [1].

The main stages of the production of ceramic, which are conventional, were reproduced in the present experiment: preparation of the initial materials in the form of nanopowders, formation the initial materials in the form of pellet-shaped blanks, heat treatment, and evaluation and analysis of the ceramic samples obtained. Pressing was done in different dies. Steel dies, 25 mm in diameter, were used at the main stage. Preliminary heat treatment of the nanoparticles and sintering were conducted in different types of furnaces,

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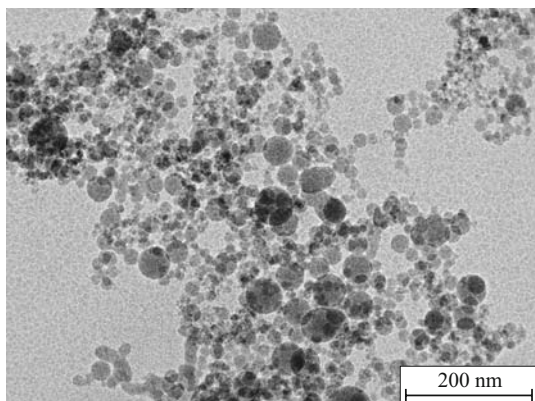


Fig. 1. Photograph of T-20 nanopowder obtained with a transmission electron microscope.

including with automatic maintenance of prescribed heating regimes.

The liquid (water) and “dry” methods of formation were used to obtain ceramic from silicon dioxide powder, and only “dry” methods of formation followed by sintering were used to obtain ceramic from hydroxyapatite powder.

In the latter case pure hydroxyapatite powder as well as a mixture of the latter with PVC-20000 polyvinyl alcohol were used as the initial material. Polyvinyl alcohol in powdered form in an amount equal to 1% of the mass of the powder was mixed with the latter. Blanks in the form of 20 mm in diameter pellets with mass 2–3 g were pressed in cycles: loading to a certain pressure on the powder, holding to deform the agglomerates and to redistribute the stresses in the pressed powder, and unloading, after which the process was repeated at a higher pressure in a time sequence; the maximum pressure in the die was 75 MPa.

The properties of the powders were studied by means of transmission (JEM-100CX, Japan; accelerating voltage 100 kV) and scanning electron microscopy, x-ray structural analysis (HZG-4 diffractometer, monochromatic Co radiation), including with the use of synchrotron radiation, by measuring the microhardness of the sintered ceramic. The shrinkage of the samples was evaluated according to the change of the geometric parameters on sintering. For comparative evaluations of gas permeability and, correspondingly, of the degree of porosity of the sintered samples, we used an apparatus in which the rate of increase of the pressure in a pre-evacuated container into which air from the atmosphere could flow through ceramic samples with the same geometry was determined by means of an electron manometer and computer. The microhardness of the sintered ceramic was measured on a PMT-3 apparatus with the surface of the sample polished beforehand. A SF-56 spectrophotometer was used to evaluate the optical properties.

Silicon Dioxide SiO_2 . Tarkosil nanopowders T-05, T-15, T-20, and T-25 [1] with specific density 50–220 m^2/g and average particle size from 13 to 60 nm were used in the pre-

sent investigations. Figure 1 shows an example of the data obtained with the transmission electron microscope for T-20 nanopowder.

Dry and wet pressing of SiO_2 powders was performed first, after which the compacts were sintered. A dense ceramic was obtained at the maximum sintering temperature 1650°C.

The indications of sintering in the dry-pressed Tarkosil samples already appeared at 1000°C with the surface and fracture surface remaining white or gray in color. Specifically, the samples did not fracture with wetting, and an examination in the scanning electron microscope showed that aggregates of sintered particles already form in them. It should be noted that the samples sintered at 1500°C already exhibited indications of vitrification. At the maximum temperature 1620°C dense ceramic formations were obtained in all cases, but these formations fragmented along layers when fractured.

When powders which were pre-moistened to a gel state were pressed, it was found that when the powder was moistened (up to water : powder ratio 1 : 1) and then loaded into the die the maximum pressing pressure at which the pellet remained uniform, did not crack, and did not demix when removed from the die increased to 26 MPa. When pure silicon dioxide powders were dry-pressed uniform blanks were obtained at pressures not exceeding 16 MPa. Apparently, wetting promotes degradation of the agglomerates, lowers the elastic stresses, and ultimately gives a more dense packing of nanoparticles in the compact. As a result, the sintered samples of both groups obtained at the temperatures indicated retained their shape, and their surfaces in most cases were smoother than for dry-pressed samples.

Although for the most part glass was not obtained from the Tarkosil powders in these investigations, a glassy state with relatively high transparency was nonetheless obtained in some samples after pressing and sintering at the maximum temperature 1550°C. Therefore, Tarkosils can be used as the initial components to obtain quartz glasses and quartz fibers. The T-05 powder (specific surface area 50 m^2/g) with very low content of OH groups on the surface and water inside the particles could be especially useful for the latter purpose. Experiments on obtaining glass with other additives show that Tarkosils can be used to prepare glass with different compositions. For example, T-20 powder (specific surface area 180 m^2/g) was mixed with boric acid in an amount equal to 5%, pressed, and sintered to maximum temperature 1300°C. The result was a strong, hard, and glass-like transparent body. However, it was brittle because it contained small bubbles.

Apparently, other modifiers will make it possible to obtain a long list of different glasses [7].

The optical properties were evaluated, using a SF-56 spectrophotometer, for one of the glass-like samples (Tarkosil T-20, sintered at 1620°C). The transparency of this sample for the visible part of the spectrum with wavelength

greater than 330 nm was worse than for window glass $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ (Fig. 2), but for wavelengths in the range 270–330 nm (ultraviolet range) the transparency of the glass obtained was better than that of window glass (for wavelengths from 330 to 270 nm the transmission of the glass obtained varied from 10% to zero, while for window glass it already dropped to zero at 320 nm and remained zero in the range 270–320 nm).

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Hydroxyapatite powder (Riedel-deHaen, Germany) with the following chemical composition was used (mass content, %): 90 $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, 8 H_2O , 0.2 HCl, 0.0002 As, 0.0001 Cd, 0.04 Fe, 0.0001 Hg, 0.0002 Pb, and 0.002 Zn. The powder contains a pure phase of hydroxyapatite (card number JCPDS 9-432), and according to x-ray structural analysis the average particle size is less than 30 nm. BET measurements were performed to obtain a preliminary estimate of the dispersity of the powder. It was found that the powder has a high specific surface area — $72 \text{ m}^2/\text{g}$.

A detailed study of the powder with a transmission microscope showed that the powder consists of agglomerates — “clusters” of submicron size, consisting of, in turn, primary particles with a predominately needle shape with maximum length less than 200 nm, transverse size of the order of several tens of nanometers, possessing a crystalline structure. On the whole the powder was indeed nanosize.

Since the maximum temperature affects the grain size, strength, and porosity, it was chosen during preliminary investigations. Specifically, it is noted in [8] that when the hydroxyapatite powder was sintered the phase composition did not change even at temperature 1400°C , although the samples did not have the maximum strength. In the present work, it was indeed found that at the maximum temperature 1500°C the samples obtained are not strong, crumble into large brittle grains, and on the whole the material of the sintered samples acquires distinct green and blue – light-blue colors. Although, x-ray phase analysis showed that the phase of the initial hydroxyapatite powder at this temperature is preserved on the whole (card 9-432). The low strength of the sample is probably due to the substantial increase of the grain size (it was determined that, in any case, the grain size is much larger than 100 nm) and simultaneously loosening as a result of the formation of a phase such as an aluminosilicate compound of calcium.

In the present work, the maximum sintering temperature varied from 1000 to 1400°C with step size 50– 100°C . In most cases the surface of the samples after sintering was smooth and became lustrous after minimal polishing. The strength parameters of the samples were not measured, but an organoleptic estimate in this temperature range shows that the samples are strong. As for the porosity, an estimate obtained by the simplest methods (specifically, according to the water absorption and water penetration through the pellet) likewise showed that it is low. At the same time the lineal shrinkage (along the diameter and height of the sample) was

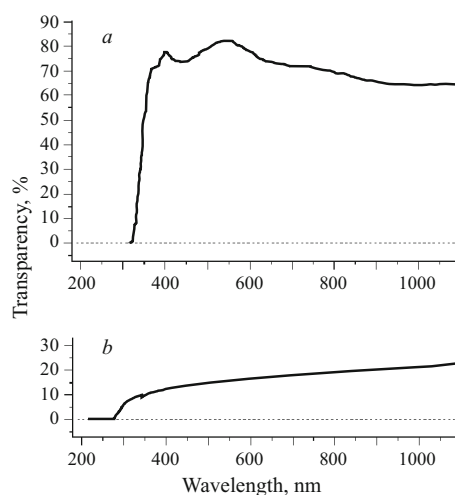


Fig. 2. Transparency (percentage transmission, according to spectrophotometer data) of window glass (a) and ceramic made from Tarkosil T-20 (b).

12–30%, and the samples apparently no longer densify much at temperatures above 1200°C . As a result of sintering, the strongest samples with a light-blue hue were obtained at the maximum temperature 1100°C . On the whole the results for the temperature range, strength, and density conform to the data of [8].

The samples sintered at the maximum temperature 1100°C was investigated in greater detail. X-ray diffraction analysis showed that the sintered samples also consisted of a pure hydroxyapatite phase (card 9-432), but the sizes of the crystallites in them, as compared with the initial powder, already exceeded 50 nm. A general survey by means of scanning electron microscopy showed that the surface of the sample after grinding, polishing, and washing was, in the main, uniform. Figure 3 displays examples of measurements made with high magnification. It is evident that the aged sample has a well-sintered continuous structure with individual pores. A general estimate of the pore size from the microscopy data shows that it is comparable to the grain size. We note that the needle structures, which comprised the initial powder on the whole, transformed into rounded grains. The internal structure can also be judged as being uniform.

The following procedures were used to obtain porous samples. The first one was based on the results obtained by some authors, showing that in a number of cases the main shrinkage of the samples occurs at the stage of increasing temperature and subsequent holding at a constant temperature makes it possible to increase the density of the ceramic by no more than 5–7%. The pre-pressed samples of hydroxyapatite which were obtained in the present work with a definite temperature regime (to fix the density and therefore the porosity to a certain degree) also contained the pure phase of hydroxyapatite. The “degree of sintering” of such samples was lower than that of samples sintered with a hold-

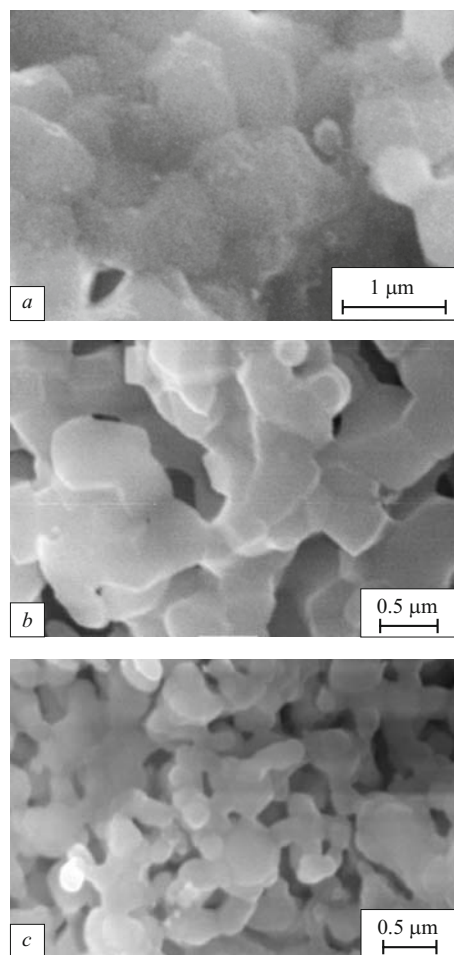


Fig. 3. Scanning electron microscope micrographs of sintered samples of nanosize hydroxyapatite powder: *a*) with aging at 1100°C; *b*) no aging at 1100°C; *c*) no aging at 1100°C, with addition of polyvinyl alcohol into the initial powder.

ing period at the maximum temperature 1100°C, and the total pore volume was appreciable larger. Very simple experiments showed that these samples already absorbed an appreciable amount of water.

Sintering samples containing polyvinyl alcohol according to the same temperature schedule showed that the alcohol burned up during the heating process but the sintered samples also possessed adequate strength. The structure obtained in the interior volume was quite uniform. On the whole the character of the porosity in the samples sintered with polyvinyl alcohol differed substantially from that of the sample obtained with aging but no additive. For the samples made using polyvinyl alcohol, water penetrated rapidly to the opposite side of the pellet.

We note that the maximum grain size in both cases was less than in the samples aged at the maximum temperature.

Experimental estimates of the gas permeability for which three curves of the variation of the pressure difference between the two sides of the samples (atmospheric on one side

and a vacuum on the other) showed the following. The samples obtained without using polyvinyl alcohol and sintered with a holding period at the maximum temperature 1100°C did not pass air. Samples without polyvinyl alcohol and no holding period at the maximum temperature 1100°C had high permeability. The highest permeability was recorded in samples which were prepared using polyvinyl alcohol. As a result it can be concluded that the gas permeability and therefore the porosity of the samples obtained by different (three) methods do indeed differ appreciably. Specifically, it can be supposed that the low gas permeability of the samples in the first group (with a holding period) is due to the formation of a large number of closed pores with size (about 1 μm and less) comparable to that of the pores in the samples from the second group. Apparently, the ceramic from the third group already has a much larger open-pore volume with an extensive pore structure; the average pore size is greater than 1 μm.

The measurements were performed primarily for samples from the first and second groups, since imprints of the correct form could not be obtained in the third group. On the whole, the microhardness of the surface was uniform, and the range of the measured values was 0.7 – 2.0 GPa depending on the sintering temperature; the maximum value was reached at the maximum temperature 1300°C.

In summary, the possibilities of obtaining ceramic from different nanodisperse silicon dioxide and hydroxyapatite powders were investigated. A fine-grain (3 – 10 μm) ceramic was obtained. The properties of the initial nanopowder and ceramic were studied by transmission and scanning electron microscopy as well as x-ray phase analysis.

The Tarkosil (silicon dioxide) nanodisperse powders with amorphous structure have lower sintering temperatures than quartz powders, and certain additives make it possible to obtain glassy materials at much lower temperatures. For wavelengths 270 – 330 nm (ultraviolet range) the transparency of the glass obtained from the Tarkosil powder was better than that of window glass (which is characteristic for quartz glass).

Strong ceramic samples with open porosity, uniformly distributed throughout the volume and with grain and pore sizes about 1 μm and less, were obtained in the experiments with hydroxyapatite nanopowder. The process of obtaining materials as modeled in the present work has certain advantages over the processes conventionally used in commercial technologies. Specifically, fewer additives (for example, binders) are used, which, ultimately, can increase the general technological level and improve the ecological cleanliness. The results obtained could be helpful for developing medical implants based on hydroxyapatite and ceramic membranes with controllable porosity.

This work was supported by the RFFI – Mongoliya 2007 – 2008 No. 07-02-90103.

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